

## The Formation and the Spread of MoO<sub>3</sub> on Au(111): Study at a Molecular Level

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*The wetting and spreading of metal oxides on catalyst surfaces is one of the important processes for the preparation of highly dispersed monolayer catalytic particles. The formation and the spread of MoO<sub>3</sub> on Au(111) has been studied using photoemission and scanning transmission microscopy (STM). Molybdenum particles (~2 nm) on Au(111) were prepared by chemical vapor deposition (CVD) of Mo(CO)<sub>6</sub> and oxidized by NO<sub>2</sub> at elevated temperatures. The MoO<sub>3</sub> spread spontaneously over the surface to form two-dimensional fractal islands of amorphous MoO<sub>3</sub>. A ramified-cluster-diffusion mechanism is proposed for the spreading of MoO<sub>3</sub>.*

The spontaneous spread of many oxides and salts over catalytic supports has been used in the chemical industry to prepare highly dispersed monolayer catalysts, and to manufacture oxide films with specific electronic properties. Scientists have been discussing the spreading mechanism of oxides for two decades, trying to explain how the monolayer-thick film forms and spreads.

We prepared a model system for investigating the formation and the spread of MoO<sub>3</sub> on a Au(111) surface. We first deposited Mo on the Au surface and found by x-ray photoemission spectroscopy (XPS) that the Mo is metallic, and free of contaminants such as carbon or oxygen. The Mo growth on the Au surface is self-limited with narrow-sized metal particles about 1.8 nm in diameter. These Mo particles aggregate without coalescence, forming ramified islands with the arms extending preferentially along the fcc troughs or the domain boundaries of the Au(111) herringbone reconstruction (**Figure 1**).

O<sub>2</sub> is not efficient for the oxidation of the Mo on Au, especially for small Mo coverages. Thus, no oxidized Mo species is observed upon the reaction with O<sub>2</sub> at temperatures up to 850 K (**Figure 2**). Density function calculations suggest that the Mo particles may be capped by a layer of Au and therefore rendered inert. However, adsorption and dissociation of NO<sub>2</sub> on metal surfaces at elevated temperatures is known to generate a reactive form of chemisorbed atomic oxygen that can oxidize the Mo clusters to MoO<sub>3</sub> at 500 K readily, as we have shown in this work (**Figure 2**). The MoO<sub>3</sub> spreads over the Au surface along the troughs of the Au(111) surface at 500 K, and the spreading becomes random at 600 K. The important finding is that the MoO<sub>3</sub> spreads in a ramified way and forms *fractal* two-dimensional islands under ultra-high vacuum (UHV) conditions. Molecule-resolved scanning transmission microscopy (STM) images show the highly disordered arrangement of the MoO<sub>3</sub> molecules within the islands; the average distance between two adjacent molecules is ~0.38 nm. The island covered area increases by a factor of six compared with the original metallic Mo/Au sample (**Figure 1**).

Previous studies have suggested three mechanisms for the spontaneous spread of MoO<sub>3</sub> over surfaces, namely transportation via gas phase, unrolling-carpet, and free surface diffusion mechanisms. These mechanisms are mutually exclusive, and neither is capable of explaining all of



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the experimental results alone. We suggest a ramified-cluster-diffusion mechanism for the spreading of  $\text{MoO}_3$ . The spread occurs via the diffusion of  $\text{MoO}_3$  clusters detached from the bulk  $\text{MoO}_3$  at temperatures above 500 K. This diffusion is a thermally activated process, and an anisotropic diffusion barrier at the edge of the island leads to the ramified spreading and the formation of the fractal islands. This mechanism explains the process of spreading on the nanoscale for all results in this and previous studies.

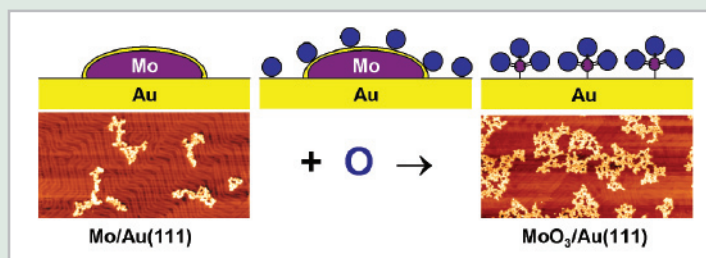


Figure 1. STM images of the Mo particles and  $\text{MoO}_3$  submonolayer film on Au(111), and cartoons for the  $\text{MoO}_3$  formation and spreading on the Au surface.

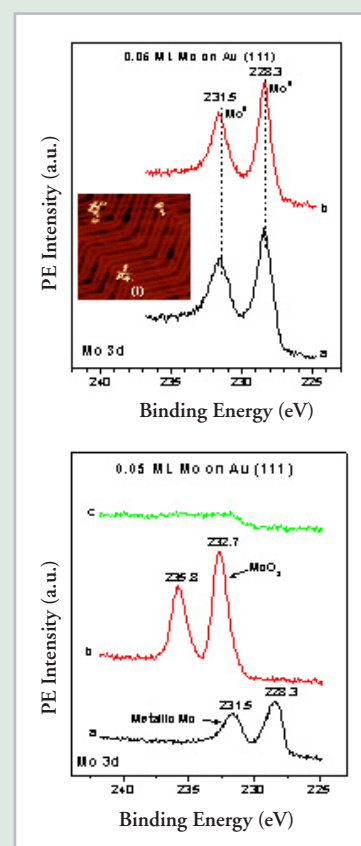


Figure 2. Mo nanoclusters after the interaction with  $\text{O}_2$  (top panel) and  $\text{NO}_2$  (bottom panel) at 500 K.